# Bench-Scale Development of a Hot Carbonate Absorption Process with Crystallization-Enabled High Pressure Stripping for Post-Combustion $CO_2$ Capture

## (DOE/NETL Agreement No. DE-FE0004360)

Illinois State Geological Survey, Prairie Research Institute, University of Illinois

Energy Commercialization, LLC

2011 DOE/NETL $CO_2$ Capture Technology Meeting

Pittsburgh, PA • August 22-26, 2011

# Project Team- Key Personnel

| | | |
|---|---|---|
| NETL | Andrew Jones | (COR) |
| ICCI | Joseph Hirschi | (ICCI manager) |
| UIUC | Yongqi Lu | (Project manager) |
| | Massoud Rostam-Abadi | (Technical advisor) |
| | David Ruther | (Laboratory specialist) |
| | Manoranjan Sahu | (Task leader) |
| | Xinlei Wang | (Prof., ABE) |
| | Xinhuai Ye | (Task leader) |
| | Two graduate students | (Research assistants) |
| Energy Commercialization, LLC | | |
| | Kevin O'Brien | (EC PI) |
| | Scott Chen | (Consultant) |
| | Askar Fahr | (Modeling) |

# Lead Contractor

- Prairie Research Institute/ University of Illinois at Urbana-Champaign
  - Five scientific surveys including Geological Survey (ISGS)
  - 700 scientists and technical support staff
  - Annual budget of $50 million
  - Lead organization of Midwest Geological Sequestration Consortium Partnership
  - Advanced Energy Technology Initiative (AETI)-ISGS
    - carbon capture & sequestration
    - materials and systems for energy and environmental applications
    - combustion-generated air pollution control
    - energy-water nexus

# Presentation Outline

- Project Overview
- Technology Fundamentals and Background
- Progress and Current Status of Project
- Plans for Future Work/Development

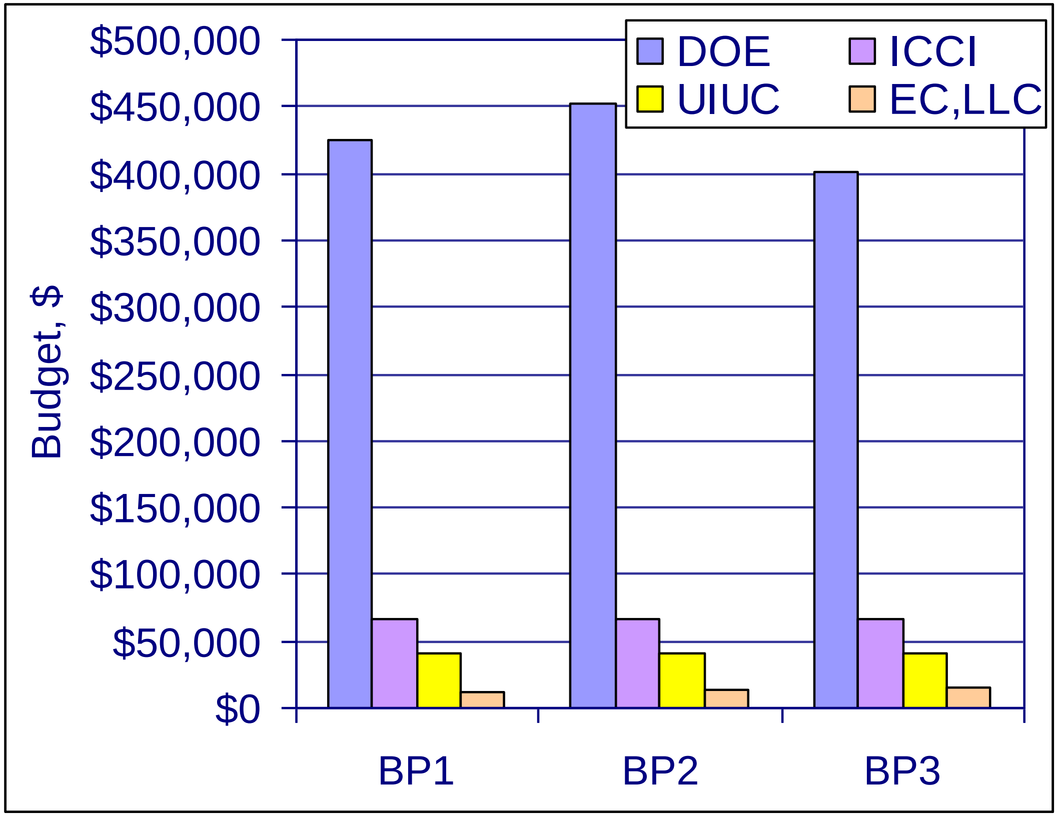
# Project Objectives

- Perform a proof-of-concept study aimed at generating process engineering and scale-up data to help advance the Hot-CAP to a pilot-scale demonstration level within three years
  - Lab- and bench-scale tests of thermodynamics and reaction engineering data of major unit operations
  - Process simulation and techno-economic analysis studies

# Project Funding

| | Budget, $ |
|---|---|
| DOE/NETL | 1,277,118 |
| ICCI (cash) | 201,000 |
| UIUC (in kind) | 124,038 |
| EC, LLC (in kind) | 40,000 |
| Total | 1,642,156 |

(Cost share is ~22%)




DOE funding and cost share on a yearly basis

Project duration: 1/1/2011 – 12/31/2013

# Project Team

DOE/NETL

- Funder

Illinois Clean Coal Institute

- Co-funder

University of Illinois at Urbana-Champaign

- Bench- and lab-scale experimental studies, co-funder

Energy Commercialization, LLC

- Process simulation and techno-economic studies, co-funder

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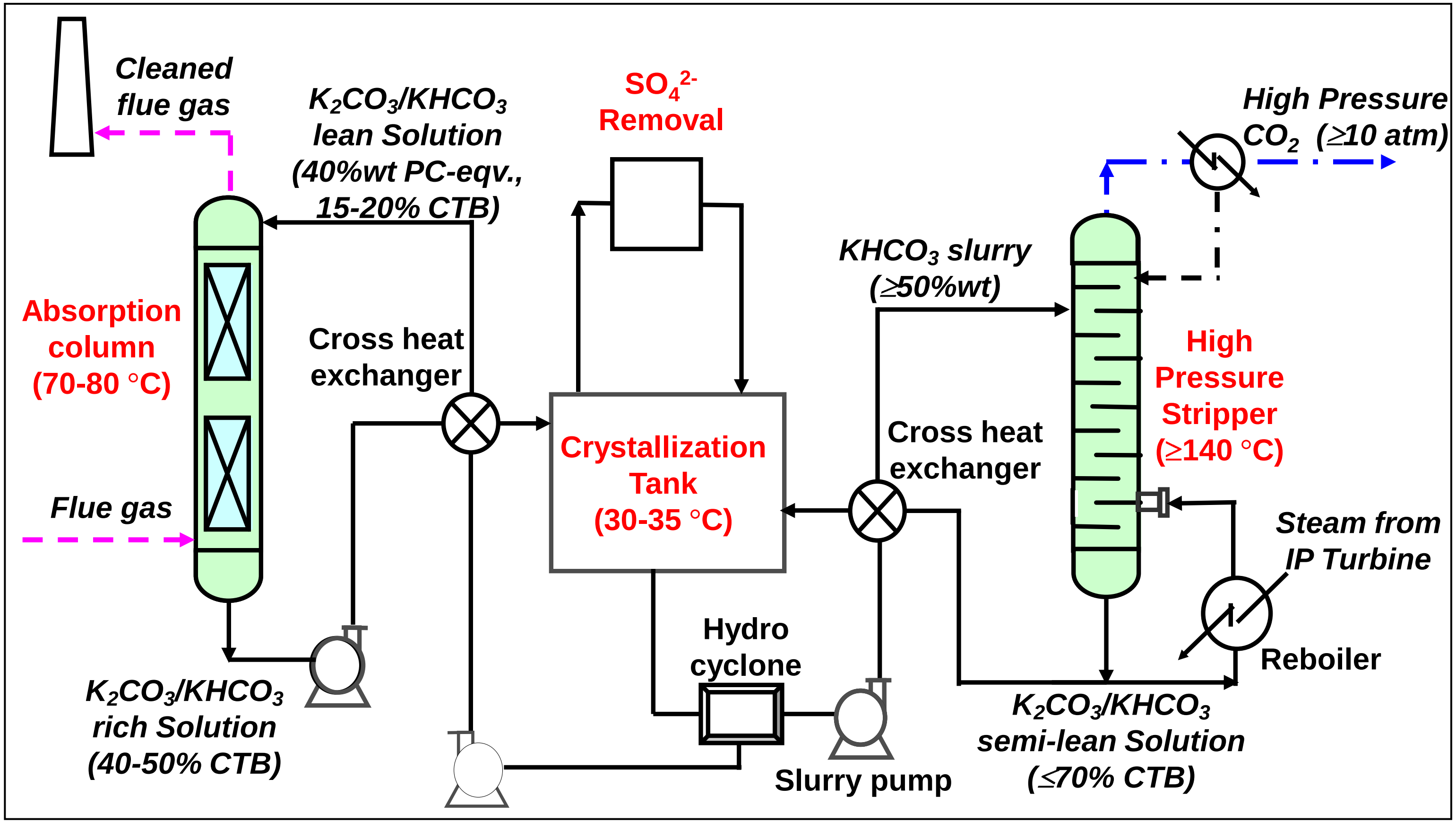
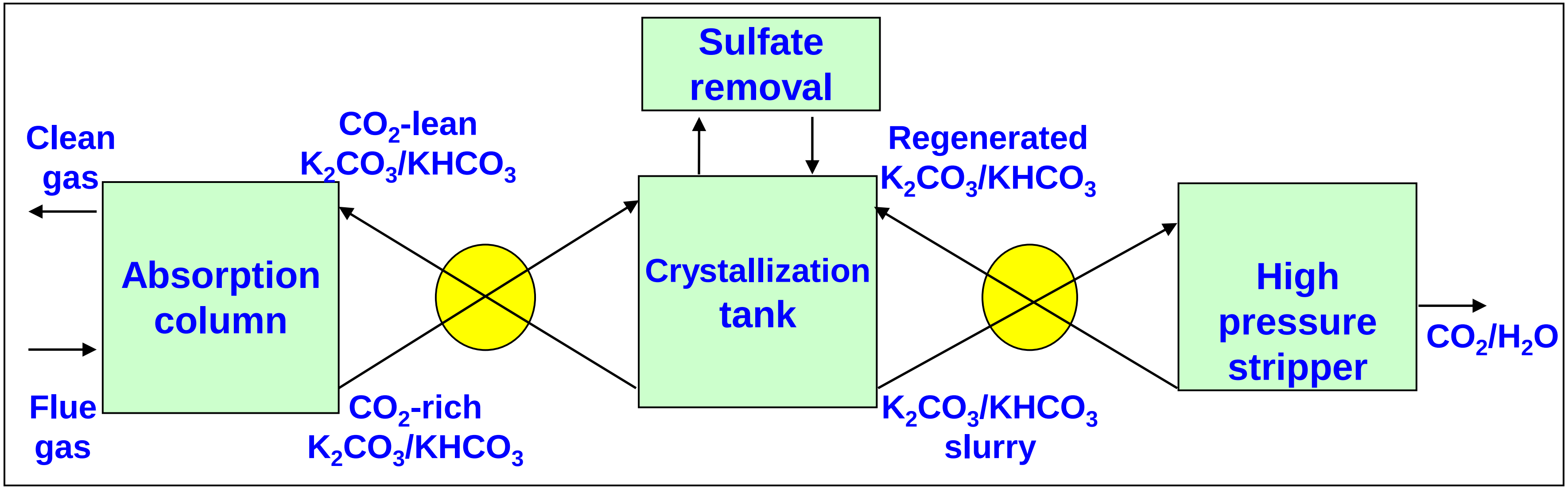
# Hot Carbonate Absorption Process with High Pressure Stripping Enabled by Crystallization (Hot-CAP): Process Flow Diagram




- Absorption at 70-80 °C
- Working capacity of 40wt% PC: ~15-40% carbonate-to-bicarbonate (CTB) conversion
- Crystallization at room temperature (~30°C)
- Stripping of bicarbonate slurry at 10-40 atm

# Major Reactions




$SO_4^{2-}$ *reclamation*

$$K_2SO_4 + CaO + 3H_2O + 2CO_2 = 2KHCO_3 + CaSO_4 \cdot 2H_2O(s)\downarrow$$

$CO_2$ *desorption at* $\geq 140°C$

$$KHCO_3 = CO_2(g)\uparrow + H_2O + K_2CO_3$$

$CO_2$ *absorption at* $70-80°C$

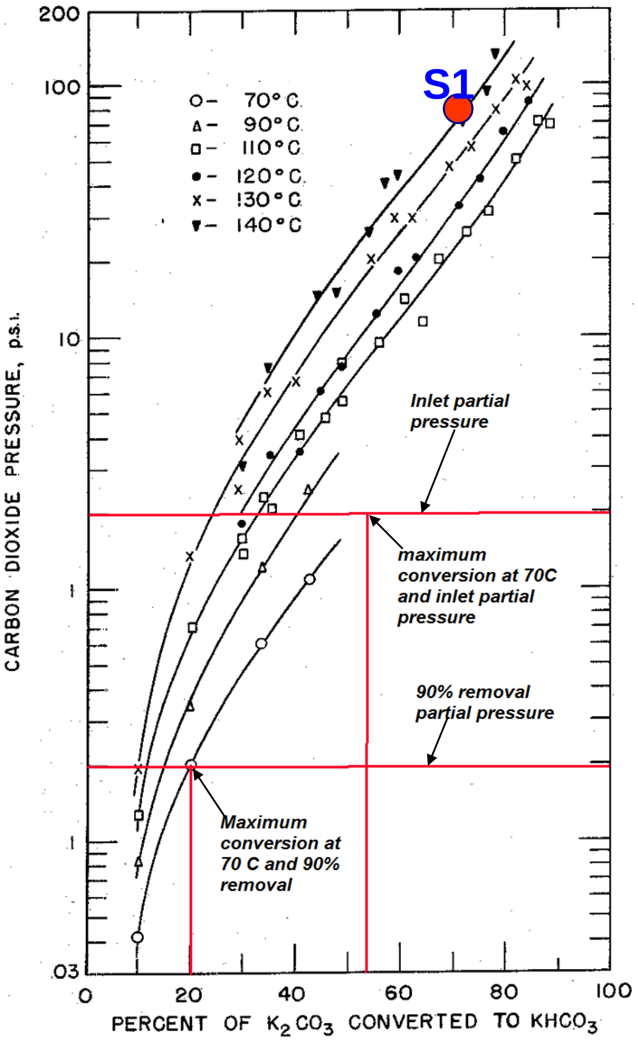
$$CO_2 + H_2O + K_2CO_3 = 2KHCO_3$$

$$SO_2 + 1/2O_2 + K_2CO_3 = K_2SO_4 + CO_2$$

*Crystallization at* $30°C$

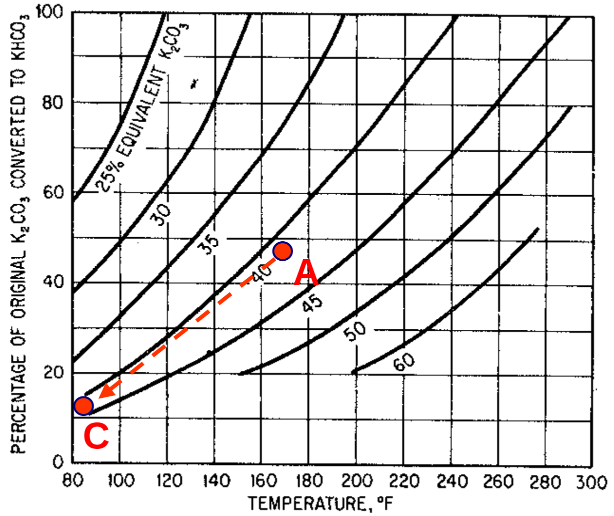
$$KHCO_3 = KHCO_3(s)\downarrow$$

# Thermodynamic Feasibility




**Vapor-liquid equilibrium of $CO_2$–$K_2CO_3$/$KHCO_3$ (40%wt) system**

- VLE data show 90% $CO_2$ removal ($P_{CO2}$=2-0.2 psia) is possible for 40%wt PC at $K_2CO_3$-to-$KHCO_3$ conversion from 15-20% at inlet to 40-53% at outlet at 70-80°C
- Higher stripping pressure (10-40 atm) possible by employing slurry (high wt%, high $K_2CO_3$-to-$KHCO_3$ conversion, see S1) and high temperature
- Bicarbonate crystallizes from A to C when cooled to ~30°C while not precipitated in absorption column (70-80 °C)




**Solubility of $KHCO_3$ in PC solution**

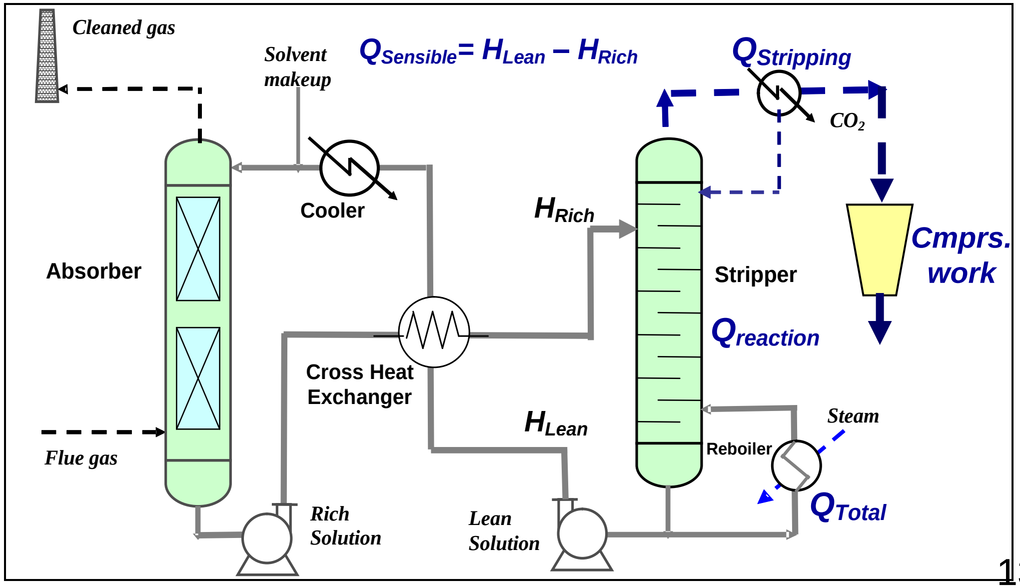
Data Source: Kohl & Nielsen. Gas Purification 5th Edit., Houston: Gulf Publishing,1997.

# Hot-CAP vs. MEA

| Items | MEA | Hot-CAP |
|---|---|---|
| Solvent | 30wt% MEA | 40wt% $K_2CO_3$ |
| Solvent degradation | Y | N |
| Corrosion | Y | Less significant |
| | | |
| Absorption temperature | 40-50 °C | 70-80 °C |
| Stripping temperature | 120 °C | 140-200 °C |
| Stripping pressure | 2 atm | 10-40 atm |
| Phase change bw absorb. and stripping | N | Crystallization |
| | | |
| FGD required | Y | N |

# Advantages of Hot-CAP

- High stripping pressure
  - Low compression work
  - Low stripping heat (high $CO_2/H_2O$ ratio)
- Low sensible heat
  - Comparable working capacity to MEA
  - Low Cp (1/2)
- Low heat of absorption
  - 7-17 kcal/mol $CO_2$ (crystallization heat incld.) vs. 21 kcal/mol for MEA
- FGD may not be required
- No solvent degradation
- Lower cost than amines
- Less corrosive than amines

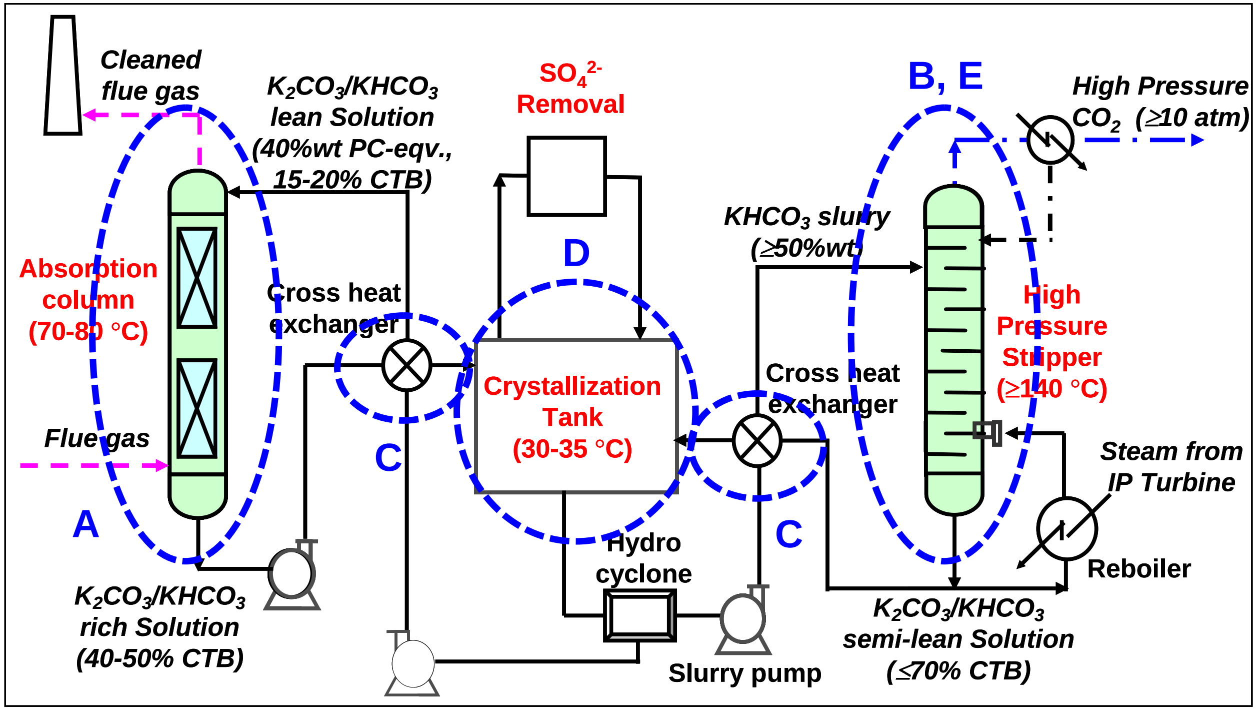


# Energy Use Comparison: Hot-CAP and MEA

| Items | MEA | Hot-CAP |
|---|---|---|
| Energy Consumption | | |
| $CO_2$ desorption | | |
| Heat of absorption (Btu/lb$CO_2$) | 825 | 600 |
| Sensible heat (Btu/lb$CO_2$) | 600 | 300 |
| Stripping heat (Btu/lb$CO_2$) | 270 | 30 |
| Electricity equivalent (kWh/ kg $CO_2$) | 0.23 | 0.17 |
| Compression work (kWh/ kg $CO_2$) | 0.10 | 0.03 |
| Total electricity (kWh/kg $CO_2$) | 0.33 | 0.20 |
| Operating | | |
| Degradation (kg MEA/ ton $CO_2$) | 2 | 0 |
| FGD Required | Y | N |

Hot-CAP system projected to have overall 40% less parasitic power than benchmark MEA system

# Technical Risks and Mitigation Strategies




| Risk | Mitigation |
|---|---|
| A. Insufficient rate of $CO_2$ absorption | Develop promoters/catalysts & reconfigure absorption column |
| B. Stripping pressure not high enough (e.g.,<10 atm) | Develop a sodium bicarbonate-based slurry |
| C. Heat exchanger and crystallizer fouling | Vender consultation, engineering analysis and customized design |
| D. Insufficient cooling rate in crystallizer affects cost/space | Same as above |
| E. Stripper required to handle slurry and high pressure | Same as above |

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# Project Tasks (1/1/2011-12/31/2013)

| | |
|---|---|
| **Task 1. Project planning & management** | **Task 4. Phase equilibrium & kinetics of high pressure <u>stripping</u>**<br>• VLE of slurry system<br>• Stripping column test |
| **Task 2. Kinetics of $CO_2$ <u>absorption</u>**<br>• Absorption kinetics<br>• Absorption column test | **Task 5. Kinetics of sulfate <u>reclamation</u>** |
| **Task 3. <u>Crystallization</u> kinetics & solubility of bicarbonate**<br>• $KHCO_3$ crystallization test<br>• $NaHCO_3$ crystallization test | **Task 6. Techno-economic <u>evaluation</u>**<br>• Risk mitigation study<br>• Process modeling/ simulation<br>• Economic evaluation |

Project currently in the 8$^{th}$ month

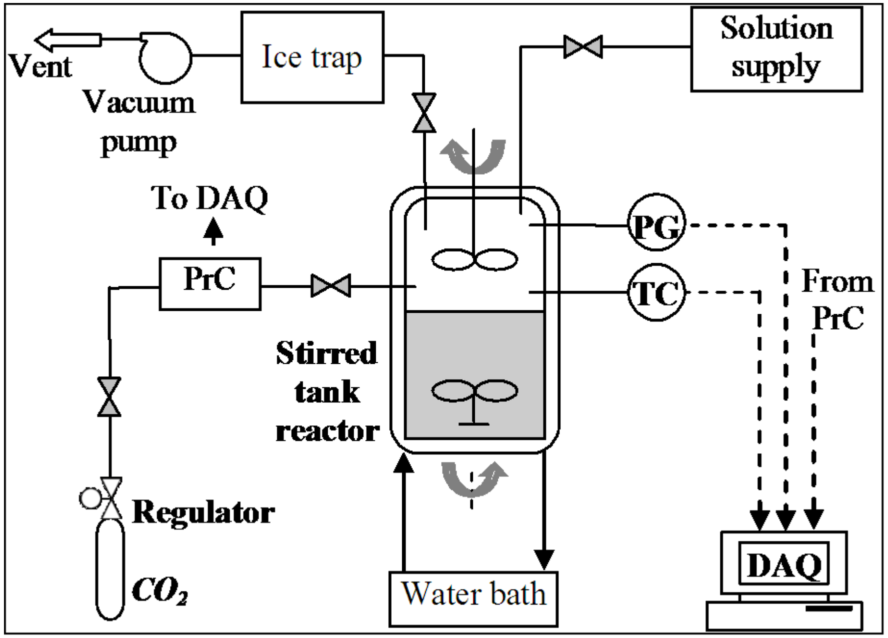
| Tasks/subtasks on project schedule | Schedule | Status |
|---|---|---|
| 2.1 Absorption in $K_2CO_3/KHCO_3$ (PC) solution | 3/1/11-12/31/11 | In progress |
| 3.1 Equipment setup & $KHCO_3$ crystallization test | 4/1/11-12/31/11 | In progress |
| 4.1 VLE of $K_2CO_3/KHCO_3$ slurry | 7/1/11-3/31/12 | In progress |
| 6.1 Risk mitigation studies and literature& data prep. | 1/1/11-12/31/13 | In progress |

# Summary of Progress to Date

Project currently in the 8th month

| Tasks/subtasks on project schedule | Comments |
|---|---|
| 2.1 Absorption in $K_2CO_3$/$KHCO_3$ (PC) solution | Results provided baseline for further promoter/catalyst and column configuration studies |
| 3.1 Equipment setup & $KHCO_3$ crystallization test | Results proved feasibility of bicarbonate crystallization at Hot-CAP conditions |
| 4.1 VLE of $K_2CO_3$/$KHCO_3$ slurry | A high pressure equilibrium cell setup is in progress |
| 6.1 Risk mitigation studies and literature & data prep. | Vendor discussions resulted in design modifications to mitigate fouling risk |

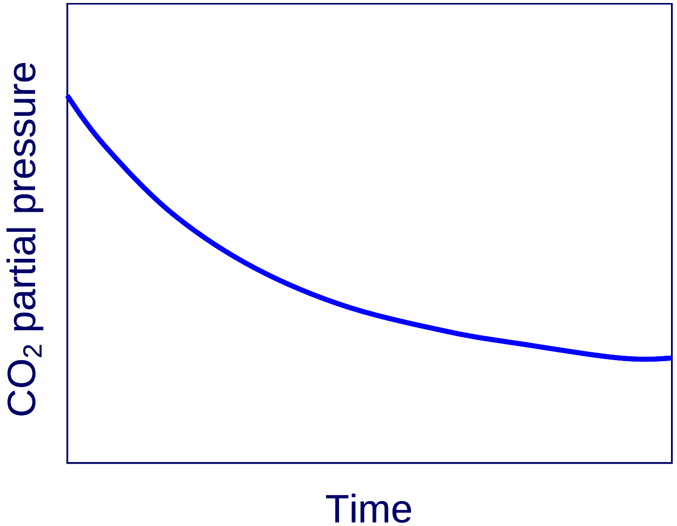
# Task 2.1 Absorption in PC solution: Stirred Tank Reactor (STR) Experimental Setup



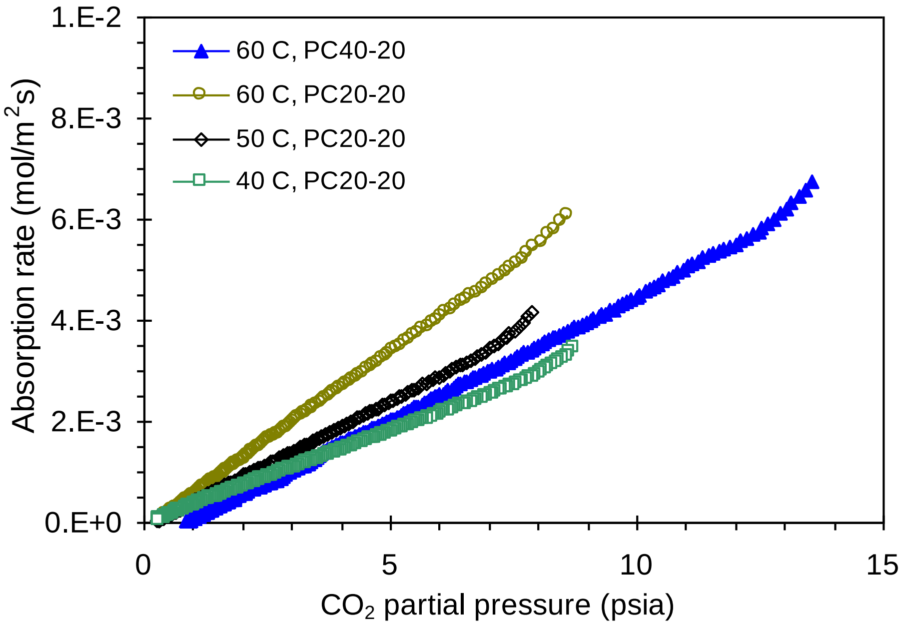

(PrC: Pressure controller; TC: Thermal couple; PG: pressure gauge DAQ: Data acquisition)

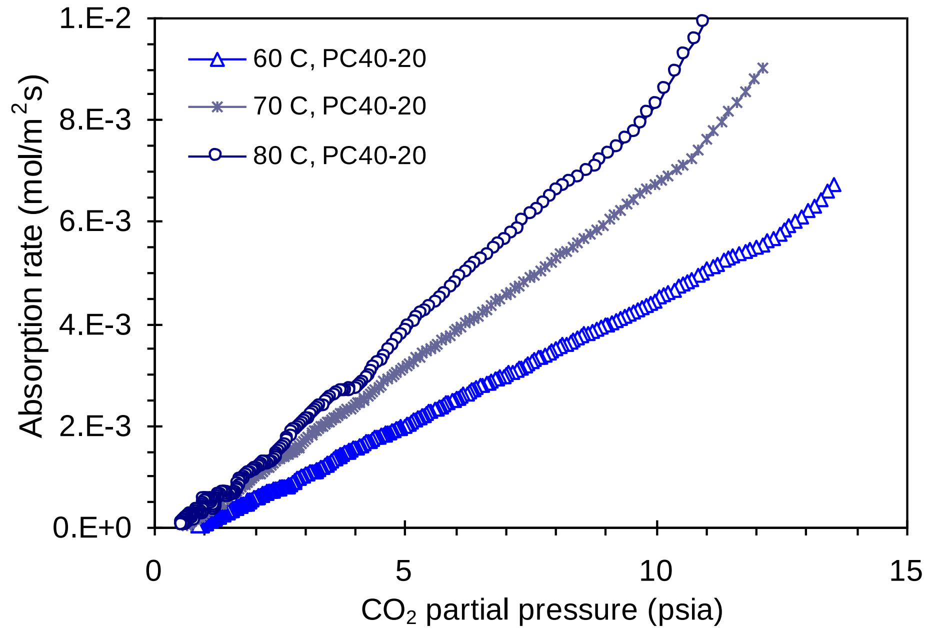
- Instant flux of $CO_2$ absorption

$$J_{CO2} = \frac{dP_{CO2}}{dt} \frac{V_g}{R\,T\,A_{GL}}$$



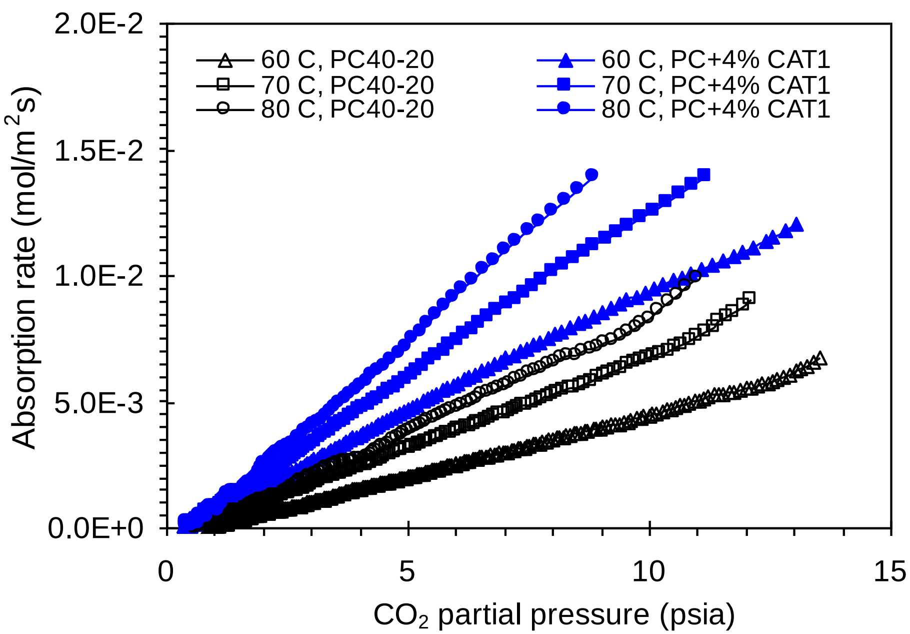
# $CO_2$ Absorption into PC Solution

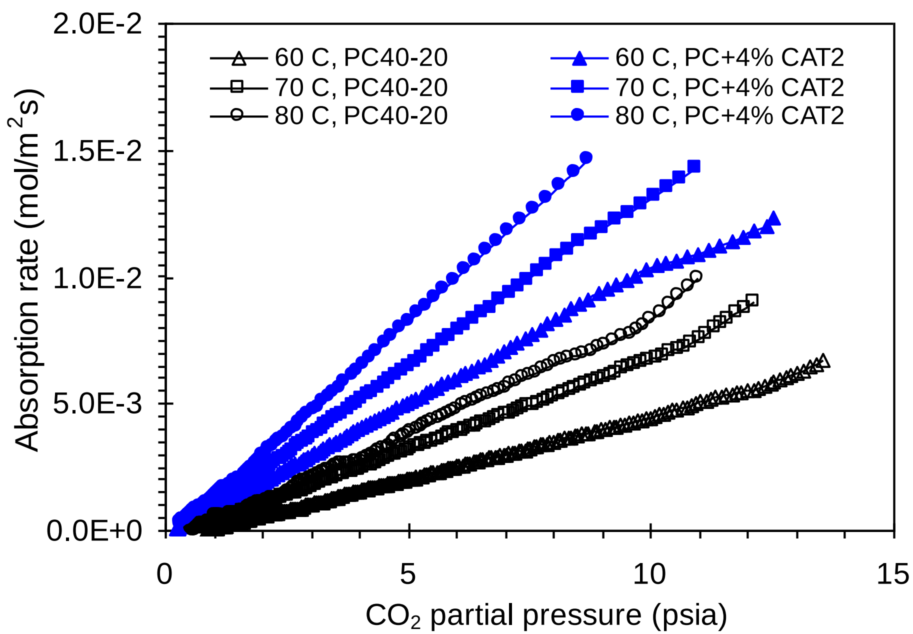



- Rates into 40wt% PC with 20% conversion (PC40-20) slower than 20wt% PC with 20% conversion (PC20-20) at the same temperature (60°C)
  - Rates adversely impacted by increasing PC concentration (impacts on diffusivity, viscosity, $CO_2$ solubility, etc)
  - Rates into PC40-20 at 60 °C still comparable to PC20-20 at 40°C and 50°C
- Rates improved by increasing reaction temperature from 60°C to 80°C
  - Impact of T on reaction kinetics > on $CO_2$ solubility (Henry’s constant)

# $CO_2$ Absorption into 40 wt% PC with Two Selected Catalysts

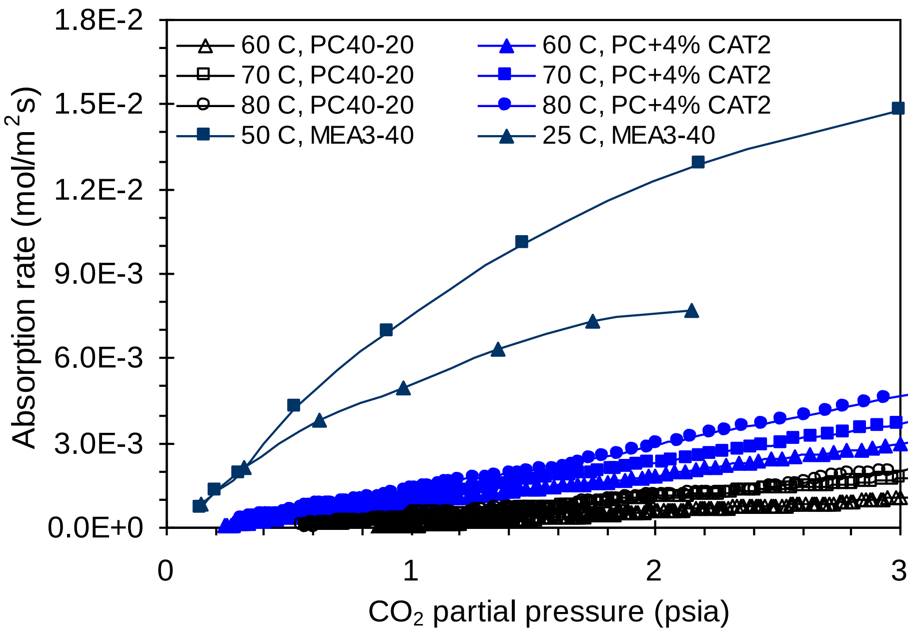



| Enhancement factor (E) | 4wt% CAT1 | 4wt% CAT2 |
|---|---|---|
| E (60°C) | 2.16 | 2.36 |
| E (70°C) | 1.86 | 2.00 |
| E (80°C) | 1.88 | 2.12 |

- Two inorganic catalysts, CAT1 and CAT2, identified more effective than other tested inorganic catalysts
- Addition of 4 wt% CAT1 or CAT2 raised rate by 2 times at 60, 70, 80°C

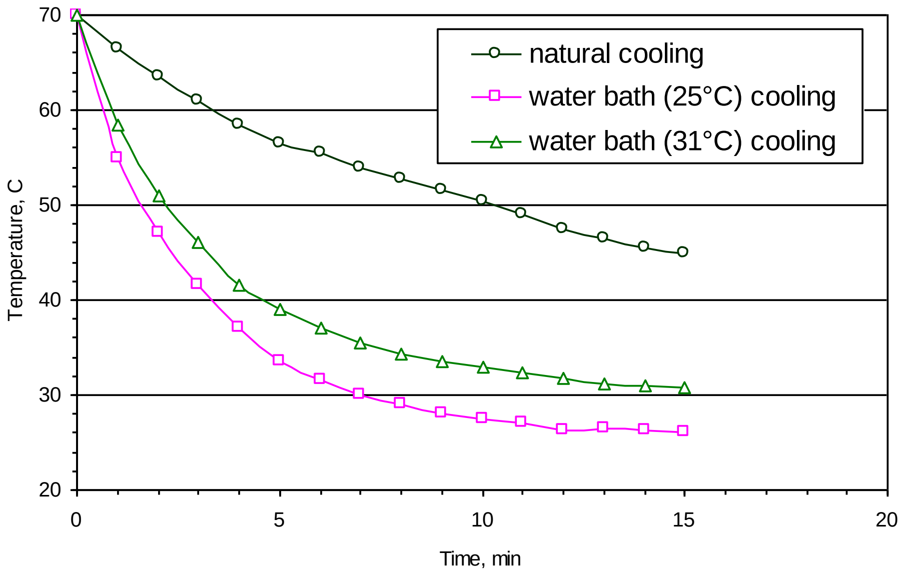
# Comparison with $CO_2$ Absorption into MEA Solution



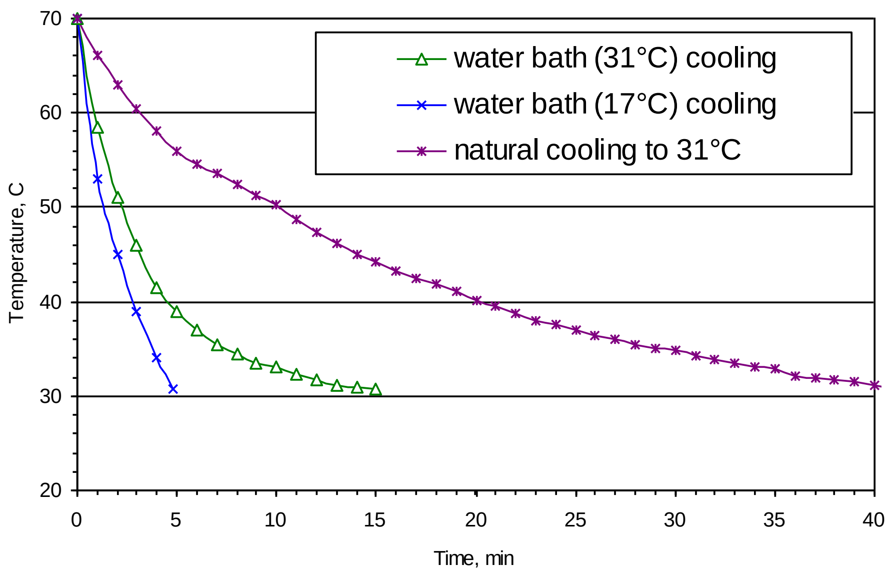

- Comparison with 3M MEA with 40% conversion (MEA3-40) at 50°C
  - STR rates into PC40-20 w/o a catalyst at 80°C were 7.1-17.9 times slower
  - Rates into PC40-20 with CAT2 at 80°C were 3.1-4.8 times slower
- Rate difference between MEA and PC40 is smaller in a packed-bed column than a STR because of the effect of gas phase diffusion
- Screening of promoters/catalysts in progress currently

# Task 3.1 Experimental Setup & Bicarbonate Crystallization

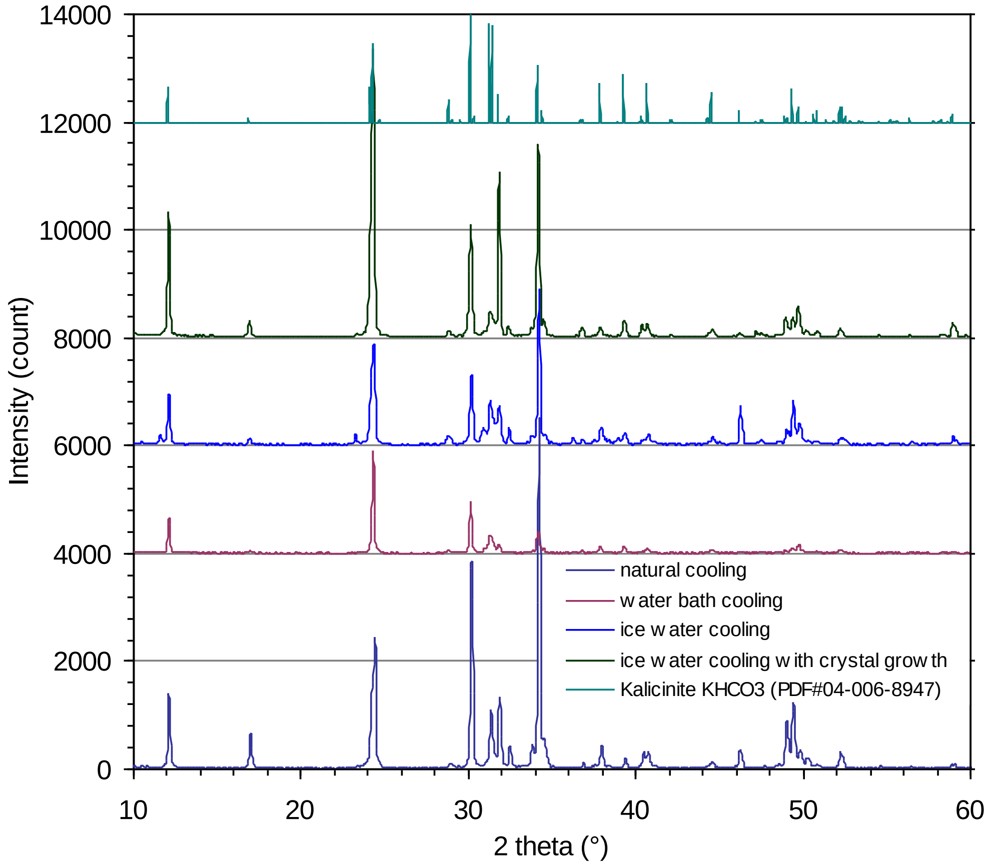
- A simplified crystallization unit
  - 100 ml reactor with stirrer
  - T control and monitoring
- 40wt% PC solution with 40% conversion (PC40-40) employed
- Starting T=70°C to end T=25-45°C

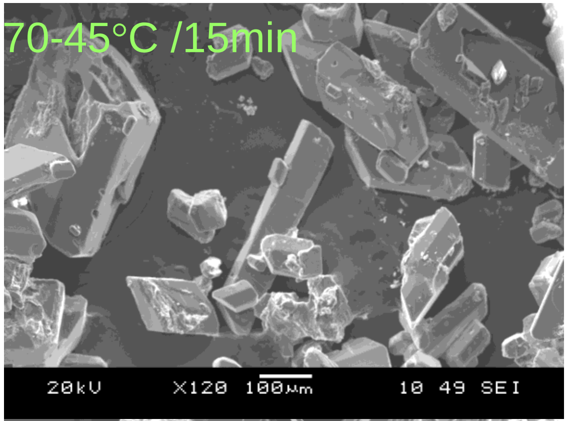


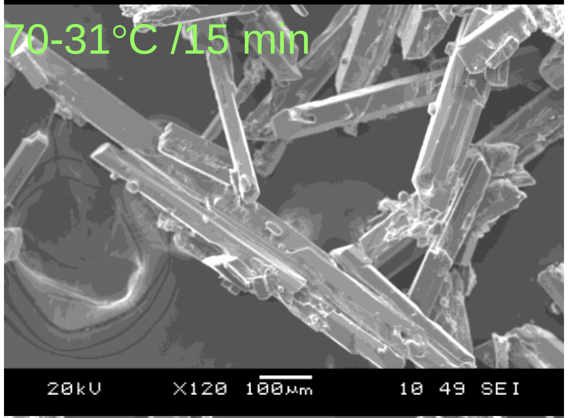

- Rate of crystallization controlled by cooling rate
  - Crystals formed immediately with decreasing T and preceded continuously
  - In rapid cooling, rate could be limited by nucleation

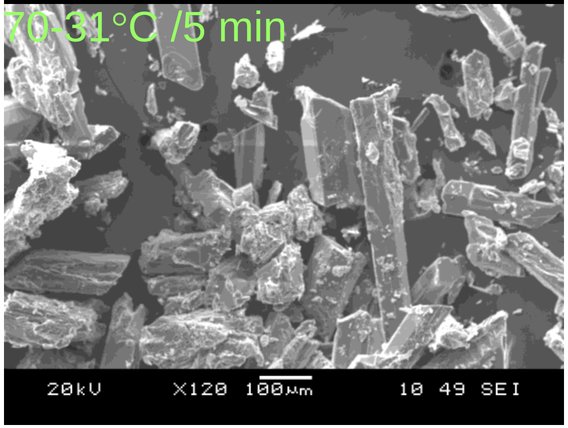


# Characterization of Crystal Products



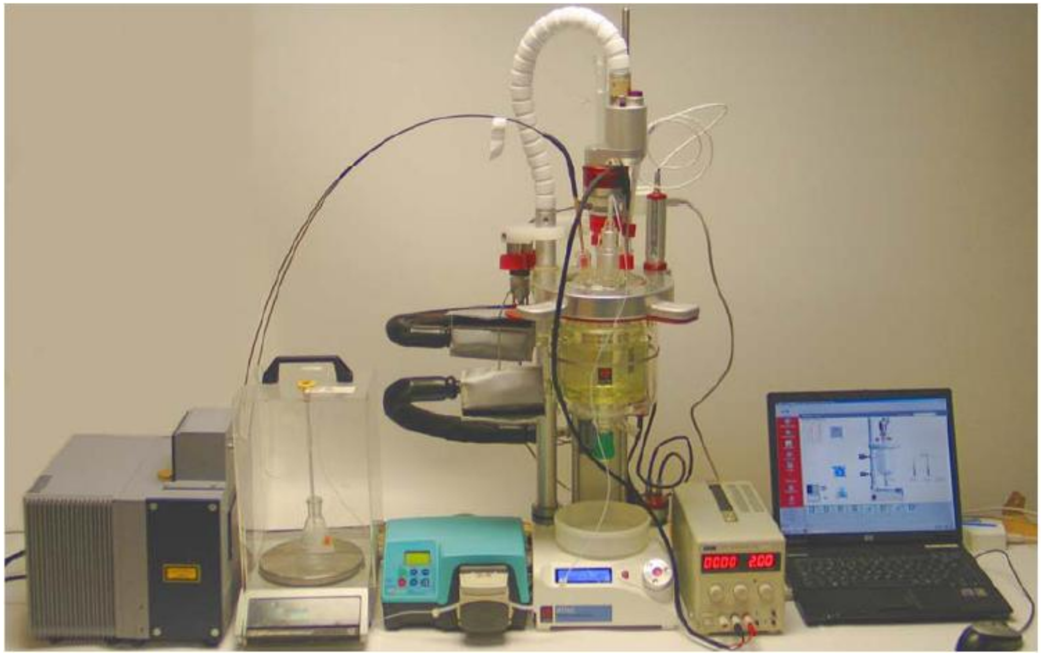




- High purity kalicinite ($KHCO_3$) prevailed in products
- More needle-shape crystals at lower cooling rate or higher supersaturation ratio
- Yield of $KHCO_3$ crystals (~50%) determined by end T

# New Experimental Setup for Crystallization



A new automated calorimetry reactor instrument (Syrris Atlas)

(accurate temperature control from -40°C -150 °C; Power Compensation Calorimetry and Heat Flow Calorimetry; turbidity and pH monitoring)

- Ongoing/ future crystallization studies
  - Crystallization kinetics
  - Optimization of product recovery (size, purity, recovery etc)
  - Crystallization heat measurements
  - Agitation effect
  - Cooling rate effect

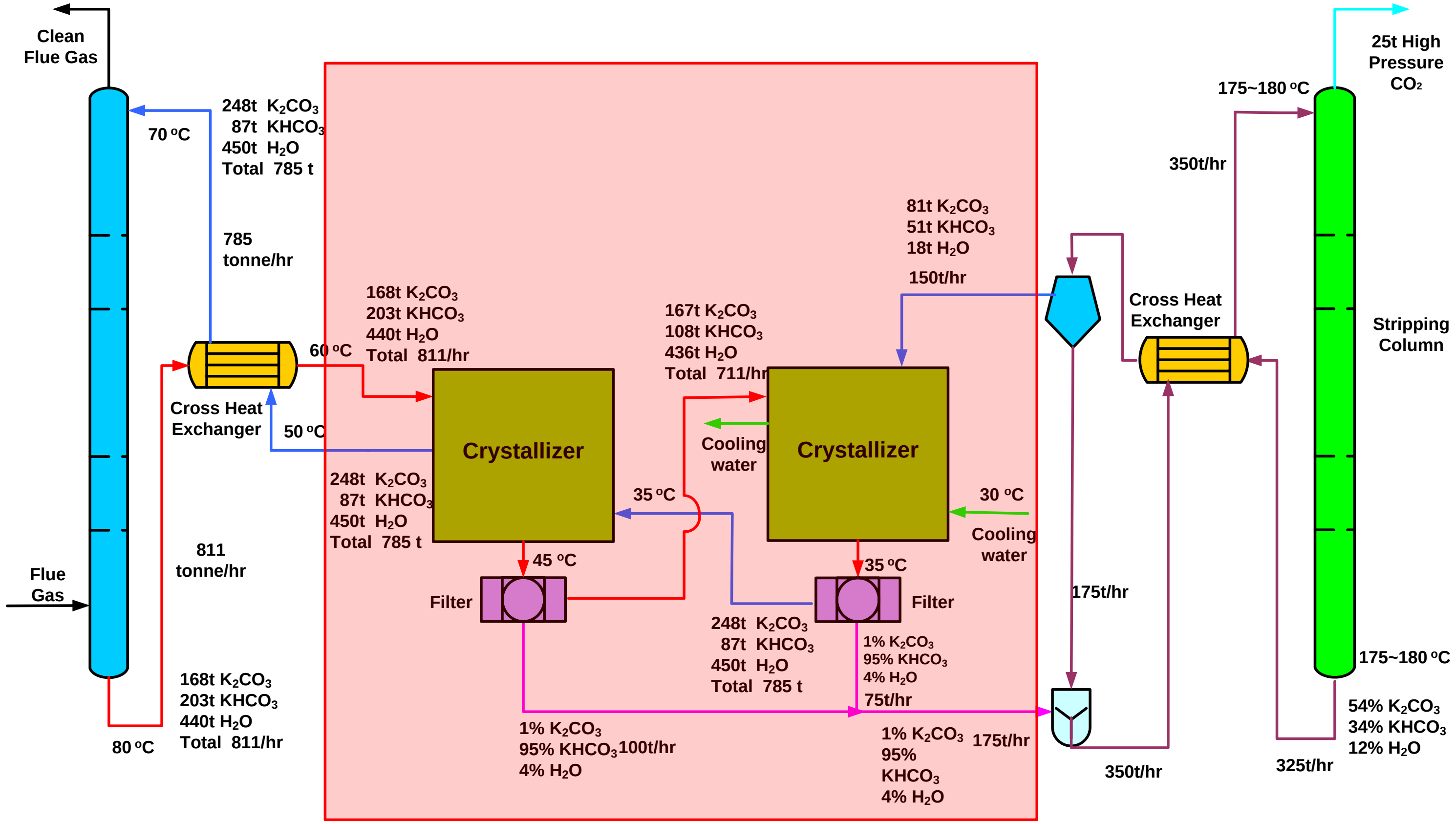
# Task 6.1 Risk Mitigation Studies – Heat Exchanger and Crystallizer's Cooler

- Options to mitigate fouling risk related to bicarbonate scaling
  - Reducing temperature difference in cross heat exchanger
  - Pre-seeding crystallization solution
  - Using plate and frame type of heat exchanger
  - Using vacuum cooling crystallizer or surface cooling crystallizer equipped with scrappers
  - Adding extra heat exchange units/modules

- Hot-CAP requires heat recovery from hot $CO_2$-rich solution from absorber

- Conventional single-crystallizer design requires a large $\Delta T$ between inlet and outlet liquids, undesirable for heat recovery from incoming solution

# Modified Crystallizer Design Option for Mitigating Fouling Risk




**(Mass balance based on a 25 MWe power plant or 25 ton/hr $CO_2$)**

- One approach is to use multiple crystallization units/modules to reduce ΔT between inlet and outlet streams of each crystallizer
- Feasibility is currently under examination by a heat exchanger vendor

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# Project Schedule (1/1/2011 – 12/31/2013)

| Budget period | BP1: 1/1/2011 – 12/31/2011 | | | | | | | | | | | | BP2: 1/1/2012 – 12/31/2012 | | | | | | | | | | | | BP3: 1/1/2013 – 12/31/2013 | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Months after contract award | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 |
| **Task 1 Project planning & management** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.1 Project planning | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.2 Laboratory preparation | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 1.3 Project management and reporting | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | Q | | | F |
| **Task 2. Kinetics of $CO_2$ absorption** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.1 Absorption in $K_2CO_3/KHCO_3$ solution | | | | a | | | | | | | | d/A | | | | | | | | | | | | | | | | | | | | | | | | |
| 2.2 Absorption in $K_2CO_3/KHCO_3/K_2SO_4$ solution | | | | | | | | | | | | | | | g | | | | | | | | | | | | | | | | | | | | | |
| 2.3 Absorption column test | | | | | | | | | | | | | | | h | | | | | | n | | | | | | | | | | | | | | | |
| 2.4 Absorption in $K_2$-$Na_2CO_3$/K-$NaHCO_3$ solution | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | t | | | | | | |
| **Task 3. Crystallization kinetics and solubility of bicarbonate** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.1 Equipment setup & $KHCO_3$ crystallization test | | | | | | b | | | | | | e | | | | | | | | | | | | | | | | | | | | | | | | |
| 3.2 Impact of sulfate on $KHCO_3$ crystallization | | | | | | | | | | | | | | | | | | j/B | | | | | | | | | | | | | | | | | | |
| 3.3 $NaHCO_3$ crystallization | | | | | | | | | | | | | | | | | | | | | | | | o | | | | | | | | | | | | |
| 3.4 Solubility of $K_2CO_3/KHCO_3$ system | | | | | | | | | | | | | | | | | | | | | | | | p | | | | | | u | | | | | | |
| **Task 4. Phase equilibrium & kinetics of high pressure stripping** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 4.1 VLE of $K_2CO_3/KHCO_3$ slurry | | | | | | | | | c | | | | | | i | | | | | | | | | | | | | | | | | | | | | |
| 4.2 VLE of $K_2CO_3/KHCO_3/K_2SO_4$ slurry | | | | | | | | | | | | | | | | | | k/C | | | | | | | | | | | | | | | | | | |
| 4.3 Stripping column test of $K_2CO_3/KHCO_3$ slurry | | | | | | | | | | | | | | | | | | | | m | | | | | | | r | | | | | | | | | |
| 4.4 Column test of $K_2CO_3/KHCO_3/K_2SO_4$ slurry | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | v | | | | | | |
| **Task 5. Kinetics of sulfate removal** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 5.1 $CaSO_4$ precipitation in $K_2CO_3/KHCO_3$ solution | | | | | | | | | | | | | | | | | | l | | | | | | | | | s/D | | | | | | | | | |
| 5.2 $CaSO_4$ precipitation in $K_2$-$Na_2CO_3$/K-$NaHCO_3$ | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | w | | | | | | |
| 5.3 Solubility of $K_2CO_3/KHCO_3/K_2SO_4$ system | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | z | | | |
| **Task 6. Techno-Economic Evaluation** | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | |
| 6.1 Literature, flowcharting & data preparation | | | | | | | | | | | | f | | | | | | | | | | | | | | | | | | | | | | | | |
| 6.2 Process modeling/simulations | | | | | | | | | | | | | | | | | | | | | | | | q | | | | | | x | | | | | | |
| 6.3 Process and economic evaluations | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | y | | | | | | |
| 6.4 Optimization & sensitivity analysis | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | aa |
| 6.5 Preparation of techno-economic study report | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | | bb |

Current date

# Research Planned in the Future

- Focus 1: Generating kinetic and phase equilibrium data using lab testing facilities
  - Promoters/catalysts for absorption
  - Kinetics and VLE data for major unit operations
- Focus 2: Bench-scale column tests
  - Absorption column test
  - High pressure stripping column test
- Focus 3: Risk mitigation studies
  - Fouling of heat exchangers in a slurry system
  - High pressure stripper design
  - Crystallizer cooler design

**End result from this project:**

**Laboratory scale system and techno-economic analysis validating technical and economic feasibility**

# Commercialization Activities

- This project
  - Continued interaction with equipment vendors to mitigate risks
  - Discussion of designs and results with engineering groups at utilities
  - Efforts designed to assure lab/bench scale system is "compatible" with power plant environment

- Next project
  - Pilot scale evaluation at field test site with slip stream

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